NASA TECHNICAL TRANSLATION NASA TT F-15,708

MASS-SPECTROMETRIC DETERMINATION OF SURFACE CONTAMINANTS

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Translation of "Mass-spektrol'noye opredeleniye poverkhnostnykh zagryazneniy," Zhurnal Analiticheskoy Khimii (USSR), Vol. 28(12), 1973, pp. 2407-2412

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 JUNE 1974

STANDARD TITLE PAGE

1. Report No. NASA TT F-15,708	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle MASS-SPECTROMETRIC DETERMINATION OF SURFACE CONTAMINANTS		5. Report Date June 1974 6. Performing Organization Code
7. Author(s) V. P. Bedrinov, V. I. Belousov, and N. V. Khromova		8. Performing Organization Report No. 10. Work Unit No.
9. Performing Organization Name and Address Leo Kanner Associates Redwood City, California 94063		11. Contract or Grant No. NASw-2481 13. Type of Report and Period Covered Translation
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration, Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

Translation of "Mass-spektrol'noye opredeleniye poverkhnostnykh zagryazneniy," Zhurnal Analiticheskoy Khimii (USSR), Vol. 28(12), 1973, pp. 2407-2412.

16. Abstract

A mass-spectrometric method has been developed for determination of overall amount of surface contamination. Accuracy of the method has been estimated by the "added-found" method, in analysis of silicon and gallium arsenide plates. The content of impurity elements on the surfaces of silicon plates after special cleaning and preservation procedures have been determined.

17. Key Words (Selected by Author(s))	18. Distribution Statement
	Unclassified-Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unclassified	10	4.00

NASA-HQ

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With the development of the film technology of semiconductor /2407* material production, monitoring of surface contaminants is becoming of special importance. It is well-known, for example, that surface impurities can pass into the epitaxial layers and change the electrophysical parameters of devices [1].

Together with chemical-spectral [2] and radioactivated [3] methods of determination of surface contaminants, the mass-spectrometric method is used, by means of which impurities of practically all elements of the periodic system can be determined simultaneously with high sensitivity ($\sim n \cdot 10^{-11}$g), without chemical etching of the layers and concentrated solutions. However, the chemical etching method, with mass-spectral completion, has significant advantages over known methods [2,3] of determination of surface contaminants. For example, it is not necessary to detach the base or chemically separate the components before analysis.

In distinction from mass-spectrometric analysis of impurities distributed through the body of a sample, in determination of the contamination content on the surface, the absolute number of impurity atoms per unit area must be known, which requires specific conditions for conduct of the experiment.

In a number of works [4-9], based on the transmission of the instrument, an extrapolated value has been found of the absolute sensitivity of the mass-spectrometric method of analysis of surface contaminants, which amounts to approximately $n \cdot 10^{10}$ atom/cm^2. Obviously, an increase in the area analyzed allows determination of lower concentrations of surface impurities.

A quantitative determination of impurities on a surface by means of a mass-spectrometer has not been carried out up to the present time, but a semiquantitative estimate of the concentration of surface contamination has been made, from results obtained in

*Numbers in the margin indicate pagination in the foreign text.

mass-spectrometric analysis of impurities distributed through the body of the sample. For a quantitative mass-spectrometric determination of surface contaminants, the method of carrying out the analysis must be improved significantly.

In this work, a type SM-602 mass-spectrometer, with a spark ion source, double focusing and photographic recording of the ions, was used. The instrument was equipped in addition with an automatic scanning system [10,11] and devices for stabilization of the interelectrode breakdown voltage [12]. The analysis was carried out automatically, by means of a programming device for sets of exposures.

Calculation of Surface Contaminant Concentrations

In a spark mass-spectrometer, the base can be used as the internal standard, which does not require calibration or comparative analysis of standard samples, as is necessary for other /2408 methods, when the quantitative content of surface impurities after their separation from the sample is determined from a calibration chart of analytical signals of the impurity elements, measured beforehand in an appropriate manner.

The vacuum spark method permits determination of the amount of surface impurities, based on the relative concentration and amount of base material used in the analysis, measured by an absolute method, for example, by weighing.

In order to put into practice the possibility of a quantitative calculation of surface impurity content, a number of conditions of the analysis must be satisfied: 1) the sequence of exposure sets should be such that they provide a reliable measurement of the densities of the analytical lines of the elements being determined in all exposures being considered; 2) scanning is carried out until complete evaporation of the surface impurities; 3) concentrations of impurity elements in the body of the sample should be quite small; 4) the transmission of the instrument should not change noticeably during the analysis.

Since the minimum depth of penetration of sparks is 0.2 μm, and the thickness of the surface contamination layer cannot exceed a few tens of angstroms (a few monolayers), the surface impurity elements are dispersed together with the base and recorded as bulk impurities with the corresponding concentrations. The characteristic of the spark discharge is such that the dispersed material is not completely removed from the discharge region. Therefore, repeated reactions of the spark with the sample are necessary, in order to completely remove the surface impurity, which permits the surface impurities to be recorded in several exposures. This is especially important in analysis of surface contaminants in high concentrations. To realize the maximum sensitivity, recording of impurities must be accomplished in a single exposure.

If, in a set of exposures E_{ico}, n_{ico} and n_{i0} atoms of contaminant and base, respectively, are dispersed, the contaminant concentration C_i (in %) is determined from the relationship

$$C_i = \frac{n_{ico}}{n_{io}} \cdot 100. \qquad (1)$$

From equation (1)

$$n_{ico} = C_i n_{i0} \cdot 0{,}01 = C_i \frac{0{,}01 \cdot P_{0i} \cdot N}{M_0}, \qquad (2)$$

where P_{0i} is the mass of n_i atoms of base, M_0 is the molecular weight of the base and N is Avogadro's number.

In a set of n exposures, the total number of contaminant atoms dispersed can be calculated from the formula

$$n_{co} = \sum_{i=1}^{n} n_{ico} = \sum_{i=1}^{n} C_i \frac{0{,}01 P_{0i} N}{M_0} = \frac{0{,}01 \cdot N}{M_0} \sum_{i=1}^{n} C_i \cdot P_{0i}, \qquad (3)$$

Assuming proportionality between the size of the set of exposures and the mass of base dispersed [13], i.e.,

$$P_{0i} = \frac{E_{ico}}{\sum E_i} \cdot P_0, \qquad (4)$$

where P_0 is the mass of base dispersed in a total set of exposures ΣE_j, we obtain from (3)

$$n_{co} = \frac{0{,}01 \cdot N \cdot P_0}{M} \sum_{l=1}^{n} C_l \frac{E_{lco}}{\sum E_j}. \qquad (5)$$ /2409

Considering that

$$C_l = K \cdot \frac{I_{\infty} M_{co}^{n,b} \cdot a_{co} \cdot I_{co}}{E_{lco}} \qquad (6)$$

we have

$$n_{\infty} = K_1 \frac{P_0}{\sum E_l} \sum_{l=1}^{n} I_{l\infty}, \qquad (7)$$

where

$$K_1 = \frac{E_0 N \delta_{co} f_{co} M_{co}^{n,b} a_{co}}{I_0 f_0 M_0^{1-b} a_0 b_0}.$$

$f_0(f_{co})$, $a_0(a_{co})$, $\delta_0(\delta_{co})$ and $I_0(I_{co})$ are the isotope factor, relative sensitivity factor, width and relative intensity of the base (contaminant) lines, respectively.

The surface contamination concentration ($\bar{n}_{co}$) is calculated from the relationship

$$\bar{n}_{co} = \frac{n_{co}}{S}, \qquad (8)$$

where S is the scanning surface.

It follows from equation (7) that the limits of detection of surface of contaminations do not depend directly on the amount of exposure, by which the intensity of the analytical lines is determined, but they are determined by the absolute sensitivity of the instrument, i.e., its transmission. However, the density of the analytical lines must be within measurable limits.

Experimental Results

For dispersion and ionization of surface contamination by a high-frequency spark, scanning of the surface was conducted with a thin counterelectrode. It was important to determine the optimum counterelectrode width, which determined the area (S) scanned back and forth. With increase in scanning area, the limits of detection of surface contaminants decrease. An increase in area can be achieved by means of increase in number of parallel scanning channels, but this complicates carrying out the analysis to a considerable extent.

TABLE 1: DEPENDENCE OF SILICON CONSUMPTION ON COUNTERELECTRODE WIDTH

Exposure, nC	Consumption, mg	Counterelectrode width, mm
1000	1.46±0.7	12
1000	1.5 ±0.7	7
1000	2.5 ±0.5	2

The dependence of amount of counterelectrode and silicon disk material dispersed on counterelectrode width was investigated (Table 1). Conditions of the analysis were: primary slit width 150 μm; pulse repetition frequency $3 \cdot 10^2$ Hz; pulse length 50 μsec; spark voltage (relative units) 4.5; accelerating voltage 25 kV. It was shown that noticeable deterioration in absolute sensitivity of the instrument does not occur with increase in counterelectrode width. Thus, in determination of surface contamination of silicon disks by the scanning method a counterelectrode approximately 12 mm/2410 wide can be used, which permits lower surface contamination detection limits to be realized without particular difficulties. As a result of subsequent investigations, whether or not the patterns obtained are observed in analysis of other materials will be determined.

To test the correctness of determination of surface contamination, standard solutions were prepared with specific concentrations

$(1\text{-}20)\cdot10^{-1}$ μg/mℓ, containing the nitrates of Cu, Bi, Pb, Hg, Ag and Te and the chlorides of Mn, Al, Mg, Fe, Cr, Sn, Ni, Ba, Zn, Sb and Ti.

A drop of each solution, with a volume of 0.04 mℓ, was applied to a silicon disk and dried under an infrared lamp. The spot forming on the surface of the disk was analyzed by the method of scanning with a silicon counterelectrode along the surface of the disk. A blank test was carried out in parallel. The conditions of the analysis were: pulse repetition frequency $3\cdot10^2$Hz; pulse length 50 μsec; ion current $2\cdot10^{-11}$ A; spark voltage (relative units) 4.5; counterelectrode cross section $0.37\cdot0.052$ cm^2 (Table 2). The concentration of the surface impurities was calculated by equations (7) and (8). The mass P_0 was determined from the results of measurement of the bulk material of the base used in sparking. Comparison with direct measurement showed that the measurement error P_0 is not over 15% by volume.

TABLE 2: SURFACE CONTAMINANT ANALYSIS CONDITIONS

Exposure Number	Exposure value, nC
1	1.10^{-1}
2	1
3	10
4	100
5	10

The results of determination of the surface contaminants introduced are presented in Table 3. From the results of three parallel analyses, the elements Mg, Ti, Cr, Zn, Ag, Sn, Sb, Te and Pb are determined with a reproducibility of approximately 30%. The coefficient of variation in determination of Fe, Cu, Mn, Ni, and Te is somewhat higher, which apparently is connected with fluctuations in the blank test level. Mercury generally was not detected. It is likely that mixing of the multicomponent chloride and nitrate solutions and their application to the silicon surface

lead , to formation of volatile mercury compounds or metallic mercury, which evaporates on drying.

TABLE 3: RESULTS OF DETERMINATION OF SURFACE CONTAMINANTS INTRODUCED TO SILICON PLATE

Element and its atomic mass	Introduced, g	Found/introduced	Blank test, g	Coefficient of variation of measurement, %
Mg 24	$9 \cdot 10^{-9}$	2,2±0.66	$1 \cdot 10^{-8}$	30
Ti 48	$1{,}8 \cdot 10^{-8}$	4.4±1.15	$3 \cdot 10^{-11}$	26
Cr 52	$9 \cdot 10^{-9}$	3,3±0.68	$1 \cdot 10^{-8}$	21
Fe 54	$4{,}5 \cdot 10^{-8}$	3.3±1.6	$8 \cdot 10^{-8}$	48
Mn 55	$4{,}5 \cdot 10^{-8}$	4±1.6	$3 \cdot 10^{-11}$	40
Ni 62	$5 \cdot 10^{-8}$	0,9±0.36	$3 \cdot 10^{-11}$	40
Cu 63	$7 \cdot 10^{-9}$	1±0.48	$1 \cdot 10^{-8}$	48
Zn 68	$9 \cdot 10^{-8}$	1±0.11	$4 \cdot 10^{-11}$	11
Ag 109	$7 \cdot 10^{-9}$	1,4±0,14	$6 \cdot 10^{-11}$	10
Sn 118	$9 \cdot 10^{-8}$	1,4±0,25	$6 \cdot 10^{-11}$	18
Sb 121	$9 \cdot 10^{-8}$	0,95±0,1	$6 \cdot 10^{-10}$	11
Te 130	$5{,}6 \cdot 10^{-8}$	0,4±0,18	$8 \cdot 10^{-10}$	45
Pb 208	$1 \cdot 10^{-7}$	1,3±0.14	$1 \cdot 10^{-10}$	11
Bi 209	$2{,}1 \cdot 10^{-7}$	0,86±0,05	$1 \cdot 10^{-10}$	6

The method discussed was used for determination of surface contamination of silicon disks (Table 4), cleaned by a special procedure (disks 1,2), as well as after their preservation (disks 3,4) with PAN-lacquer, a 5% solution of polyacrylonitrile in dimethyl formamide. It is clear from the data in Table 4 that the silicon disks contain a considerable amount of surface contamination. The presence of chromium apparently is connected with contamination of the disks during their treatment with chromium-base pastes.

Since the coefficients of relative sensitivity to K, Ca, and /2411
Na can differ considerably from unity, amounts of them were introduced only for a relative comparison. After preservation with PAN-lacquer, the amount of surface contaminants increased somewhat.

TABLE 4: ANALYSIS OF SURFACE CONTAMINANTS OF SILICON DISKS

Disk No.	Element content, atom/cm^2							
	K	Ca	Mg	Cl	Cu	Cr	Na	Fe
1	$6\cdot10^{15}$	$1\cdot10^{14}$	$1\cdot10^{15}$	$3\cdot10^{15}$	$3\cdot10^{13}$	$7\cdot10^{13}$	$9\cdot10^{14}$	$3\cdot10^{14}$
2	$8\cdot10^{15}$	$1\cdot10^{14}$	$8\cdot10^{14}$	$3\cdot10^{14}$	$1\cdot10^{15}$	$1\cdot10^{15}$	$1\cdot10^{15}$	$2\cdot10^{14}$
3	$7\cdot10^{15}$	$2\cdot10^{14}$	$1\cdot10^{15}$	$5\cdot10^{15}$	$1\cdot10^{13}$	$5\cdot10^{13}$	$9\cdot10^{15}$	$3\cdot10^{14}$
4	$3\cdot10^{16}$	$7\cdot10^{14}$	$2\cdot10^{15}$	$3\cdot10^{16}$	$1\cdot10^{14}$	$4\cdot10^{14}$	$2\cdot10^{16}$	$2\cdot10^{15}$

The correctness of determination of the impurity element content on the surface of gallium arsenide plates was tested by means of analysis of previously sputtered copper. Copper sputtering was carried out in a UVN-1 unit, by the method of [14,15]. The analysis was carried out, using a counterelectrode of low-resistance germanium alloyed with gallium. The counterelectrode cross section was 0.35 x 0.03 cm^2.

TABLE 5: CONDITIONS OF ANALYSIS ON GALLIUM ARSENIDE PLATES

Exposure Number	Exposure value, nC
1	10
2	100
3	30
4	10

Since the fraction of germanium in the spectrum amounts to several percent and the copper content in it is less than the detection limit, in calculation of the copper concentration, the contribution of germanium was not taken into account. Conditions of the analysis were: pulse repetition frequency $3\cdot10^2$ Hz; pulse length 50 μsec; ion current $4\cdot10^{-11}$ A; spark voltage (relative units) 3; primary slit width 150 μm (Table 5). The results of the analysis are presented in Table 6. The amount of copper found on the surface of the gallium arsenide plate by the mass-spectrometric method coincides with that introduced, within the limits of error of the measurement.

TABLE 6: RESULTS OF ANALYSIS ON GALLIUM ARSENIDE PLATES

Exposure value, nC	Introduced by sputtering, g	Atomic mass	Found, g	Detection limit, g
150	$1 \cdot 10^{-10} \pm 0.5 \cdot 10^{-10}$	Cu^{63} Cu^{65}	$1,7 \cdot 10^{-10} \pm 0,5 \cdot 10^{-10}$ $1,7 \cdot 10^{-10} \pm 0,5 \cdot 10^{-10}$	$8 \cdot 10^{-12}$

The method proposed of determination of impurity concentrations on the surface can be used for analysis of liquids containing impurities of low volatility. Besides, it can be used for monitoring cleanliness of a surface after carrying out the appropriate cleaning operations of solid samples.

Conclusions

A mass-spectrometric method of determination of the absolute quantity of surface contaminants has been developed. The correctness of the method has been established by the "added-found" method, in analysis of silicon and gallium arsenide plates. The content of impurity elements on the surface of the silicon after a special cleaning and preservation procedure was determined.

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